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GEOCHEMISTRY

Gold and Platinum Group Metals in Skarns of the Ol'ginsk and Dal'negorsk Ore Districts of Primorye and Some Issues of Metallogeny of the Southern Sikhote Alin Region

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The Triassic–Jurassic carbonaceous sequence of Sikhote Alin includes metalliferous sediments represented by siliceous–rhodochrosite rocks and their metamorphosed analogues [3, 4], siliceous rocks with pyrophanite ("brown cherts"), tin–iron ores, "ilmenite–biotite–feldspar" (metamorphosed clayey) rocks, and "itabirites." They are characterized by high contents of Au, Ag, Pt, and Pd [2] and the ubiquitous presence of minerals of these elements. Hydrothermally altered sandstones, as well as siliceous–clayey and siliceous rocks, which are associated with syngenetic metalliferous rocks, contain grains of gold, silver, argentite, platinum, Pd-platinum, itenbohaardite, and other minerals of noble metals. It should be mentioned that identifications of all minerals mentioned in this paper have been confirmed by microprobe analyses. Another type of hydrothermal ores is represented by Mn-rich amphibole–pyroxene rocks that contain native gold, silver, Pd-platinum, and other minerals of gold, silver, and platinum group metals (PGM). Hydrothermal ores are products of the regeneration of metalliferous rocks due to the evolution of Late Cretaceous granitoid massifs. The amphibole–pyroxene rocks formed after calcareous sandstones, which are probably of Late Triassic age [3].

The southern Sikhote Alin region incorporates numerous Late Cretaceous skarn and vein (cavity-filling) deposits of lead, zinc, silver, tin, tungsten, and iron. Skarns are characterized by high concentrations of Mn derived from manganese rocks [1]. Similarly as other metalliferous rocks, the manganese rocks are enriched in Pb, Zn, Ag, Sn, W, and Fe. Hydrothermal deposits of these metals define the metallogenic profile of the southern Sikhote Alin region. Manganese and other metals mentioned above were probably derived from metalliferous rocks of the Triassic–Jurassic carbonaceous sequence.

The metalliferous rocks and associated hydrothermal rocks contain Au and PGM. For example, these metals are concentrated in amphibole–pyroxene rocks of the Shirokaya Pad area of the Ol'ginsk district. These rocks are analogues of the adjacent manganiferous skarns of the Belogorsk skarn magnetite deposit in all aspects except the protolith (calcareous sandstones rather than limestones). Therefore, one can also expect the presence of Au and PGM in skarns of the Belogorsk deposit and other skarn deposits of the Ol'ginsk and Dal'negorsk ore districts. In order to check this assumption, we investigated skarns of the Skal'naya (Skal'nyi Otvod) and Blagodatnaya lodes (Belogorsk deposit), as well as the Dal'negorsk borosilicate and Sadovoe skarn base metal deposits.

The *Skal'nyi Otvod lode* is mainly composed of bustamite, mangansalite, garnet, and manganactinolite. Apatite and barite are subordinate. One can see microscopic sphalerite, galena, anglesite, arsenopyrite, cassiterite, wolframite, zincite, bismite, chalcocite, silver sulfate, löllingite, stannite, ilsemannite, and native zinc. Solid solutions of various metals, such as Cu–Zn–Pb, Cu–Zn–Pb–Sn, Cu–Sn, Cu–Pb–Cd, W–Co–Cr–Ti, W–Co–Rh, Bi–Ag, and Bi–Pb–Ag, are widespread. The rock contains grains of "cupriferous gold," i.e., members of the Cu(Au,Ag)–Cu_2(Au,Ag) isomorphous series (Table 1). In addition, the rock contains numerous inclusions of native gold (diameter up to 2.0 μm) with traces of Cu (and/or Ag) and less abundant native platinum (diameter 1–4 μm, up to 3 × 8 μm in size). One can also see native silver grains, single grains of

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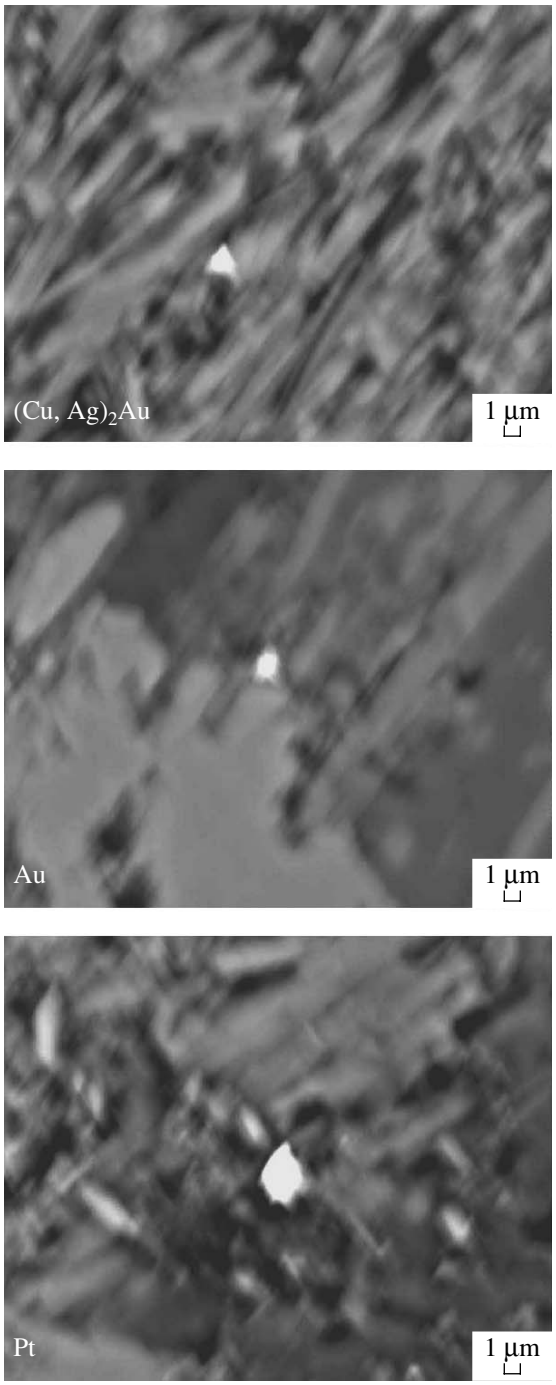
cinnabar, coloradaite, $In_{0.91}(PO_4)_{1.09}$, Pd-platinum, and native(?) rhenium. The sum total in analyses shows a departure (sometimes significant) from 100% due to the small size of grains, and numerous cavities or carbonates are present near the grains analyzed. Nevertheless, the analyses are well recalculated to stoichiometric formulas of the respective minerals.

The *Blagodatnaya lode*, initially composed of Mn- and Sn-bearing garnets, Mn-clinopyroxene, and a small amount of Zn-bearing magnetite, was reworked by hydrothermal solutions [1]. The relatively less altered pyroxene–garnet skarn of this lode contains carbonate, quartz, bismuth minerals, and apatite. Microscopic inclusions consist of wolframite, scheelite, cassiterite, barite, chalcopyrite, pyrite, arsenopyrite, gudmundite, antimonite, and native iron and nickel, as well as solid solution Cu–Zn; $Ag_{1.02}Cu_{1.90}Sb_{1.08}S_{4.01}$; and other compounds of Cu, Ag, Pb, and Sb (Table 1). Silver mainly occurs as argentite. One can also see grains of $Ru(Pb, Ag)_2Bi_4$, native platinum (with traces of Cu in some places), and native gold (pure or with traces of Cu, Ag, Co, and less common Pt in some places).

The *Dal'negorsk borosilicate deposit* incorporates lodes of pyroxene–wollastonite skarn replaced in some places by the danburite–datolite ore. The pyroxene–wollastonite skarn includes tiny (*n*–10*n* μm) grains of barite, wolframite, scheelite, cassiterite, zircon, monazite, baddeleyite, native tungsten and zinc, and solid solutions (Cu–Zn, Cu–Zn–Pb, Cu–Zn–Sn, Cu–Sn, Co–W, and Ni–Cu). One can also see grains of cinnabar, uraninite, vaesite, $CuAg_6S_4$, intermetallic compounds of the $Ni_2(Fe,Cr)$ type, and cupriferous gold (Fig. 1). The rock contains Ag mainly as a native mineral and argentite. One can also see native gold (pure or Ag-rich) and ferroplatinum (Table 2).

The *Sadovoe deposit* is a proxy of the group of skarn base metal deposits in the Dal'negorsk ore district. The hedenbergite skarn contains inclusions of galena, pyrrhotite, wolframite, scheelite, cassiterite, zircon, barite, and oxides of various metals (Zr, Ti, Sc, Sr, Ce, and Th). The rock also includes native iron, antimony, zinc, and tungsten; intermetallic compounds $Fe_3(Cr,Ni)$, $(Fe,V,Cr)_2Ti$, and Fe_2Ce; and solid solutions Cu–Zn, Cu–Zn–Pb, Cu–Zn–Sn, Cu–Zn–Ni, Ni–Cr, and Co–W (Table 2). One can see grains of cotunnite, jemsonite, and rooseveltite. The rock contains Ag (argentite or $Cu_{1.00}Ag_{1.96}S_{2.04}$ and $Cu_{0.98}Ag_{3.95}S_{3.07}$), Au, Rh, and other PGMs. Gold occurs as cupriferous or native minerals.

Thus, irrespective of the iron, base metal, or boron mineral composition of ores, skarns of the Ol'ginsk and Dal'negorsk ore districts of Primorye contain minerals of Au, Ag, and PGM. The results of atomic absorption analysis show that the skarns are enriched in Au, Pt, and Pd.* They are distinguished from the metalliferous rocks by the high Pd/(Au + Pt) ratio (Table 3). Therefore, skarn deposits of Primorye should be checked for the contents of Au and PGM irrespective of the type of major mineralization in them. The unaltered and weakly altered skarns are most interesting in this respect. Both skarns and metalliferous rocks are characterized by the presence of organic matter, an abundance of NaCl and KCl, reduced forms of metals (20 metals in the native



Cupriferous gold, native gold, and ferroplatinum (bright sectors) in the pyroxene–wollastonite skarn of the Dal'negorsk borosilicate deposit.

* After the submission of this paper, we detected in skarn of the Sadovoe deposit a mineral of Pd represented by Pd_3Ag (according to analysis, $Pd_{2.98}Ag_{1.02}$).

Table 1. Results of the microprobe analysis of minerals from skarns of the Belogorsk deposit

Ord. no.	O	Mg	Al	Si	S	Ca	Cr	Mn	Fe	Cl
Skal'naya lode										
1	42.67		8.88	15.36		16.73		2.71	2.62	
2	0.99	0.34		1.12					0.67	
3	13.72	0.99		6.07		3.28	3.02	1.16	11.99	
4	14.88	0.74	3.73	7.02		10.35	2.35	1.26	4.01	
5	42.20	1.53		31.27	2.86	2.78		0.89	5.47	
6	12.49			3.36		1.30	1.04		16.52	
7	14.91			1.95		1.26	2.22	0.90	3.54	1.05
8	35.56			31.77		0.64			0.45	
9	13.51			1.51		26.74	1.45	1.64	0.83	
Blagodatnaya lode										
10	29.06	0.24	0.72	0.92		28.43		0.31	0.46	
11	28.13	2.24		4.86		10.54		6.55	2.46	
12	10.72					10.64		1.82	1.15	
13	26.55					21.78		3.09	0.71	
14	30.24	0.55	1.29	13.55	5.31	2.69			0.87	1.43
15	7.54				20.14				12.54	
16	2.64				11.57	0.30			0.50	
17					15.50					
18	17.41		0.26	0.33		0.87			39.01	
19	16.29					0.22	0.58		45.12	

Ord. no.	Cu	Zn	Ag	Re	Pd	Pt	Au	Pb	Bi	Total
Skal'naya lode										
1					3.66	7.81				100.44
2			101.33							104.45
3		1.38				59.62				101.23
4	8.98		2.19				16.6			72.11
5			1.00					6.04	9.35	103.39
6		3.32					62.17			100.20
7			2.46				71.01			99.30
8			1.31						16.68	86.41
9				7.33						53.01
Blagodatnaya lode										
10						0.81	12.64			91.46
11							42.95			97.73
12	1.54		5.48				66.31			97.66
13			2.12					12.05	32.09	102.04
14			39.23							100.00
15	19.46		16.34							98.11
16		1.01	8.09					33.88	35.65	93.50
17		3.35	9.84					25.37	49.82	103.88
18	0.66					41.43				99.97
19	2.36						35.68			100.25

Note: (1) $Pd_{0.46}Pt_{0.54}$; (2) native silver; (3) native platinum; (4) cupriferous gold $Cu_{0.57}Au_{0.35}Ag_{0.08}$; (5) $Ag_{1.86}Pb_{5.93}Bi_{9.07}S_{18.14}$; (6) pure gold $Au_{1.00}$; (7) gold $Au_{0.94}Ag_{0.06}$; (8) $Bi_{0.87}Ag_{0.13}$; (9) native(?) rhenium; (10) gold $Au_{0.94}Pt_{0.06}$ (additional components, wt %: 13.10 P, 3.96 F, 0.83 Na); (11) pure gold $Au_{1.00}$, (12) gold $Au_{0.82}Ag_{0.12}Cu_{0.06}$; (13) $Ru_{0.98}(Pb_{1.54}Ag_{0.49})_{2.03}Bi_{3.88}$ (3.65 Ru); (14) argentite $Ag_{2.06}S_{0.94}$ (0.52 Ti, 4.32 Na); (15) $Ag_{5.02}Cu_{10.15}Sb_{6.01}S_{20.82}$ (22.09 Sb); (16) $Ag_{0.88}Pb_{1.91}Bi_{1.99}S_{4.22}$; (17) benjaminite $Ag_{0.76}Pb_{1.02}Bi_{1.98}S_{4.00}$; (18) platinum $Pt_{0.95}Cu_{0.05}$; (19) gold $Au_{0.83}Cu_{0.17}$. Here and in Table 2, the table shows the whole-rock composition in the case of small grains due to contamination with the surrounding rock mass. The presence of Cr in many analyses is related to contamination with Cr_2O_3 used for polishing. Analyses were carried out using a JXA8100 microprobe equipped with three wave spectrometers and an INCAx-sight energy-dispersive spectrometer at the Far East Geological Institute, Vladivostok.

Table 2. Results of the microprobe analysis of minerals from skarns of the Dal'negorsk deposit

Ord. no	O	Mg	Al	Si	S	Ca	Mn	Fe	Ni	Cu	Zn	Ag	Rh	Ce	Pt	Au	W	Pb	Total
Pyroxene–wollastonite skarn of the Dal'negorsk borosilicate deposit																			
1	9.79			5.96		5.59	1.24	1.59				70.07							94.24
2	17.45	0.34		8.82	8.34	7.60	1.97	3.18		0.81		45.49							94.00
3	6.05			2.20		3.06	0.51	7.34							80.17				99.33
4	32.98		0.43	19.37		19.98	3.55	4.31				2.64				16.08			99.34
5	23.43	0.24		20.42		26.53	3.61	4.71								16.14			97.08
6	21.41		0.90	16.79		17.16	2.29	2.95		14.33		2.53				21.23			99.59
7	21.63			21.19		1.42	0.56	0.95									54.17		99.92
8	11.58			13.63		10.01	2.12	3.52	47.17	3.75									91.78
9	7.29			3.30	12.97	3.32	0.74	0.91		6.45		64.54							99.52
Manganhedenbergite skarn of the Sadovoe deposit																			
10	28.59	0.32	0.43	8.28	8.53	5.72	1.24	6.16				49.55							109.28
11	15.49	0.29	0.30	10.87		9.66	2.10	10.32								35.81			84.84
12	17.77		2.63	10.07		8.04	2.01	12.40		12.75						18.80			84.47
13	21.30		1.51	10.58		5.21	1.25	6.70		18.87		5.43				35.74			106.60
14	10.46			2.77		2.17	0.65	2.96					1.03					55.75	76.44
15	8.99		0.77	1.36		1.03				33.39	33.82							13.11	92.47
16	10.47	0.36	0.73	10.82		4.35	2.37	6.28	6.25	29.88	28.92								101.80
17	15.61		2.11			2.67	0.64	3.91									72.70		103.46
18	8.74		0.47	7.59		4.03		35.69						41.22					98.01

Note: (1) Silver; (2) argentite $(Au_{1.82}Cu_{0.05})_{1.87}S_{1.12}$; (3) ferroplatinum $Pt_{0.76}Fe_{0.24}$ in wollastonite; (4) gold $Au_{0.77}Ag_{0.23}$; (5) pure gold $Au_{1.00}$; (6) cupriferous gold $Cu_{0.63}Au_{0.30}Ag_{0.07}$; (7) tungsten; (8) $Ni_{0.93}Cu_{0.07}$ in pyroxene; (9) $Cu_{1.01}Ag_{5.96}S_{4.03}$; (10) argentite $Ag_{1.90}S_{1.10}$ (additional components, wt %: 0.45 Na); (11) gold; (12) cupriferous gold $Cu_{0.67}Au_{0.33}$; (13) cupriferous gold $Cu_{0.56}Au_{0.34}Ag_{0.10}$; (14) minium(?) in pyroxene (0.64 Cl); (15) $Cu_{0.48}Zn_{0.47}Pb_{0.05}$; (16) $Cu_{0.46}Zn_{0.43}Ni_{0.11}$ (0.26 K, 1.11 Cl); (17) $Co_{0.20}W_{0.80}$ (5.82 Co); (18) $Fe_{1.94}Ce_{1.06}$ (0.26 Cl).

Table 3. Analysis of skarns of manganese rocks from the Ol'ginsk and Dal'negorsk ore districts by the atomic absorption method (g/t)

Ord. no.	Sample no.	Au	Pt	Pd	Pd/Au + Pt	Au + Pt + Pd
1	Sd-1	0.54*	0.83	5.34	3.90	6.71
2	Bs-1	0.73	0.81	1.78	1.16	3.32
3	B-79-22	0.20	0.84	0.78	0.75	1.82
4	B-79-86	0.91	1.54	2.35	0.96	4.80
5	S-8	0.19	1.50	0.19	0.11	1.88
6	S-10	0.35	0.51	n.d.	0.00	0.86
7	S-11	0.38	0.49	n.d.	0.00	0.87
8	S-13	2.48	11.27	2.12	0.15	15.87

Note: (1–4) Skarns: (1) Sadovoe deposit, (2) Dal'negorsk borosilicate deposit, (3, 4) Blagodatnaya lode (Belogorsk deposit); (5–8) manganese rocks exposed in the Sadovoe deposit; (*) Au up to 3.35 g/t based on the fire assay analysis (Laboratory for the Analysis of Noble Metals, Far East Geological Institute, Vladivostok). Methodological features: acid decomposition of samples, reduction of noble metals by $SnCl_2$, concentration on metallic tellurium, and determination in a graphite cuvette (V.F. Zanina and V.N. Zalevskaya, analysts). (n.d.) Not detected.

state, more than 100 varieties of solid solutions and intermetallic compounds, including phosphides, silicides, and nitrides, in addition to, probably, borides), and the presence of cupriferous gold. We believe that Mn in skarn deposits was derived from manganese rocks, while Fe could mainly be derived from "itabirites." Other metals, such as Pb, Zn, Sn, W, Ag, Au, and PGM, could be derived from metalliferous rocks of all types developed in the Triassic–Jurassic carbonaceous sequences of Sikhote Alin.

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